

Teacher's Tools[®] Chemistry

Electrochemistry: Voltaic Cells: Student Review Notes

Cell Voltages: Standard Cell Potentials

The value of the Cell Voltage or Reaction Potential (they mean the same thing) is the driving force behind the redox reaction.

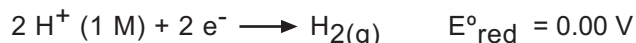
Cell voltage depends upon (1) the nature of the redox reaction
(2) the concentration of the species involved in the reaction

Standard reduction potentials have been tabulated for the reduction of many of the species you will see involved in redox reactions. Note: only the reduction potential (E°_{red}) is given on these tables. The potential associated with the reverse reaction, the oxidation potential (E°_{ox}) is the negative of E°_{red} . Also, if the reaction you are examining is a multiple of the one you find on the table, **DO NOT** multiply E°_{red} by the associated constant. **Potential is like the height of a waterfall, the number of electrons you flow over the waterfall does not change the height of the waterfall.**

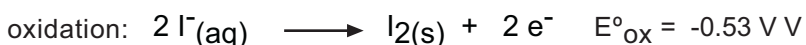
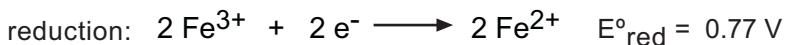
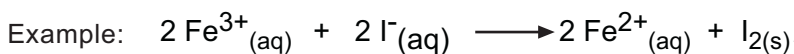
“Standard“ means: 1 M solutions of ions or molecules and a pressure of 1 atm.

$$E^\circ_{\text{ox}} + E^\circ_{\text{red}} = E^\circ_{\text{total}} = \text{the standard potential for the redox reaction}$$

The tabulated half-reaction redox potentials are measured in reference to the reduction of hydrogen cation. This is the **arbitrary zero point** established for the reduction potential scale.



Determining E°_{tot} for a redox reaction.



$$E^\circ_{\text{ox}} + E^\circ_{\text{red}} = E^\circ_{\text{total}} = 0.24 \text{ V}$$

iron goes from +3 to +2 that is a gain of electrons or reduction
iodine goes from -1 to 0 that is a loss of electrons or oxidation

go to the table of standard reduction potentials and find the reactions. Remember to reverse the reaction for iodine since it is oxidation. Also, remember to **NOT** multiply the half reaction potentials by stoichiometric coefficients.

Determining the strength of oxidizing/reducing agents

Oxidizing agents gain electrons, they get reduced \longrightarrow the **more positive E°_{red} the stronger the ox. agent**

Reducing agents lose electrons, they get oxidized \longrightarrow the **more positive E°_{ox} the stronger the red. agent**

In the previous example, iron(III) cation was the oxidizing agent and iodine anion was the reducing agent.

If you look at a table of standard reduction potentials, you'll see that diatomic fluorine is the strongest oxidizing agent and solid lithium metal is the strongest reducing agent. That should make sense to you based on where these atoms reside on the periodic table and the octet rule.

Spontaneity of Redox Reactions

One reason that electrochemistry is interesting is that it is a class of reactions, redox reactions, for which thermodynamic data and thus equilibrium data can be experimentally obtained.

Here is how it is tied together:

We know from thermodynamics that $\Delta G = \Delta H - T\Delta S$ and $\Delta G^\circ = -RT\ln K$

Electrochemistry allows us to directly measure the change in Gibbs Free Energy according to:

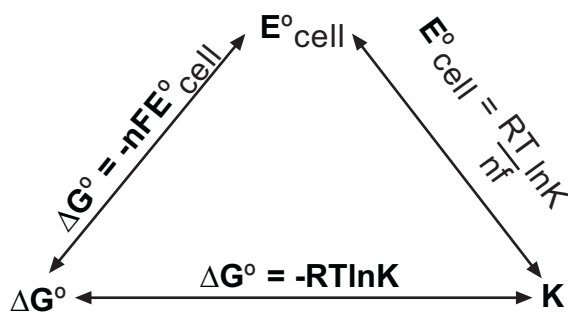
$$\Delta G^\circ = -nFE^\circ$$

n = the number of moles of electrons transferred in the reaction

F = the Faraday constant, 96,500 C and it is the charge of 1 mole of electrons in Coulombs.

E° = the standard cell potential.

Now, we can relate ΔG° , E° and K . And, E° is a quantity that is relatively easy to measure experimentally.



It is very important that you understand how to move between these different quantities.

Electrochemistry is tied to Thermodynamics and Thermodynamics determines chemical equilibrium.

BTW, E°_{cell} is the same thing as E°_{tot}

Accordingly, we can look at the sign of E° and its relation to ΔG° to determine the spontaneity of a redox reaction.

$\Delta G < 0$ indicates that a **chemical reaction is spontaneous**

$\Delta G = 0$ indicates that a **reaction is at equilibrium**

$\Delta G > 0$ Indicates that the **reverse reaction is spontaneous**

$$\Delta G^\circ = -nFE^\circ_{\text{tot}}$$

$E^\circ_{\text{tot}} > 0$ indicates that a **redox reaction is spontaneous** and can be used in a **Voltaic Cell**

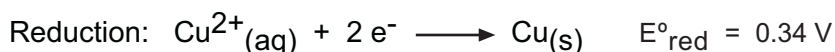
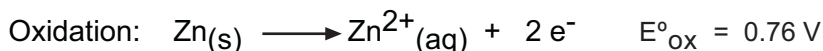
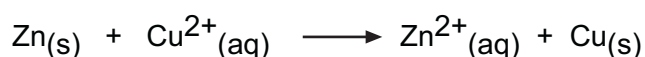
$E^\circ_{\text{tot}} = 0$ indicates that a **redox reaction is at equilibrium**

$E^\circ_{\text{tot}} < 0$ Indicates that the **redox reaction is non-spontaneous**. This is where we use an **Electrolytic Cell**. In an electrolytic cell a voltage of at least E°_{tot} is supplied.

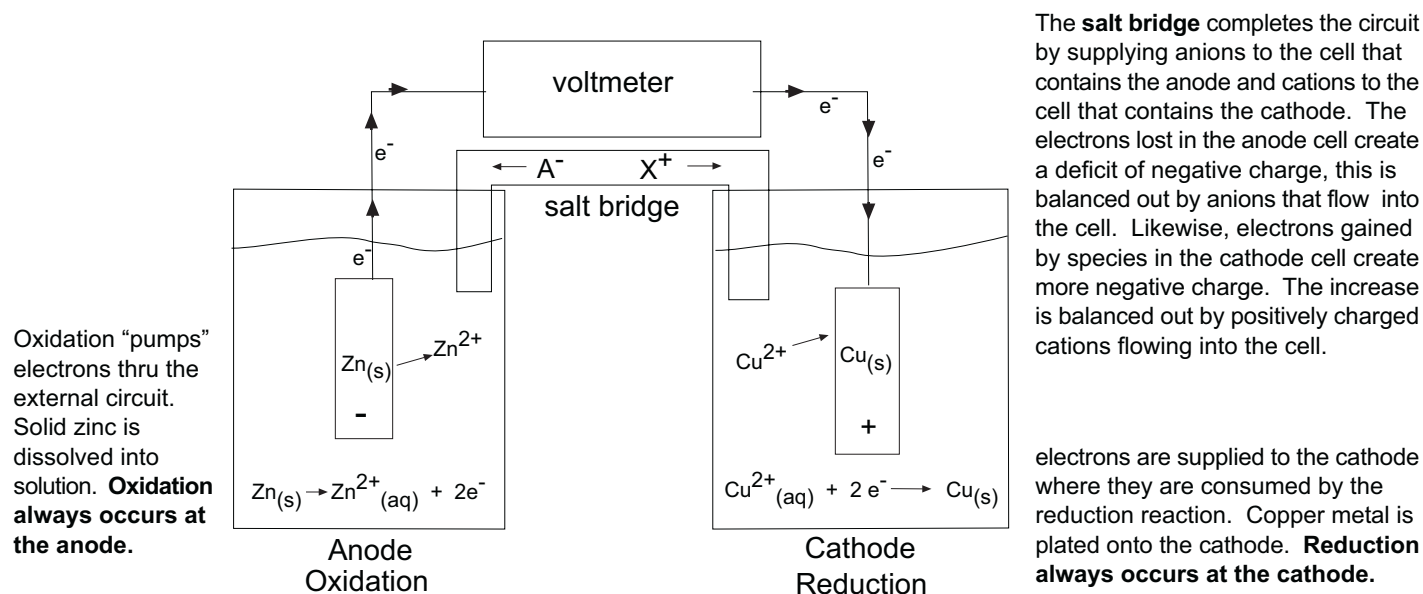
The Voltaic Cell

$E^{\circ}_{\text{tot}} > 0$ in a **Voltaic Cell**. The reactants will react spontaneously. What we do is put them in separate cells and then complete the circuit or connection between the cells. This allows electrons to be transferred in accordance with the spontaneity of the reaction. The cells act like an electron pump--oxidation pumps electrons through to reduction. You can also think of like setting up two pools of water and a waterfall between them. The species that is oxidized is in the higher pool and the one reduced is in the lower pool.

This "pump" drives the flow of electron or current and we've made a battery. The passage of electrical current can be used to do mechanical work. Let's take a look at how this is set up for a spontaneous redox reaction. We'll use solid zinc metal and copper(II) cation. **This combination is called the Daniell Cell.**

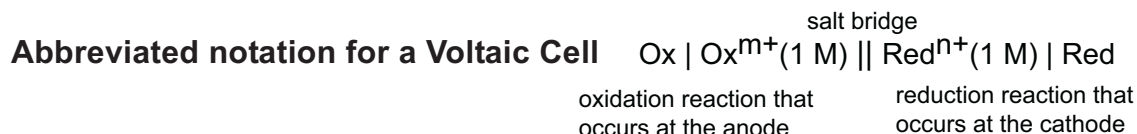


$$E^{\circ}_{\text{cell}} = 1.10 \text{ V} > 0 \text{ so its spontaneous}$$



Know this:

	<u>ANODE</u>	<u>CATHODE</u>
ions attracted	anions(-)	cations(+)
how electrons move	into the anode out of the cell	into the cell/out of the cathode
half-reaction	Oxidation	Reduction
electrode Sign		
Voltaic Cell	negative	positive
Electrolytic Cell	positive	negative



Always indicate the concentrations in each cell. If an inert metal electrode like platinum is used, put the name of the metal in parenthesis next to the appropriate reactant. For example, if the redox couple was zinc metal and hydrogen cation and a platinum electrode was used in the hydrogen cell at standard conditions the abbreviated cell notation would be:



Concentration Dependence of a Voltaic Cell

Qualitatively, the effect of concentration of cell potential follows Le Chatelier's Principle.

If the concentration of the **reactants** in the equilibrium constant expression **increases**, that pushes the reaction in the **forward** direction, the reaction becomes **more spontaneous** and the **reaction potential increases**.

If the concentration of the **products** in the equilibrium constant expression **decreases**, that pushes the reaction in the **forward** direction, the reaction becomes **more spontaneous** and the **reaction potential increases**.

Likewise,

If the concentration of the **reactants** in the equilibrium constant expression **decreases**, that pushes the reaction in the **reverse** direction, the reaction becomes **less spontaneous** and the **reaction potential decreases**.

If the concentration of the **products** in the equilibrium constant expression **increases**, that pushes the reaction in the **reverse** direction, the reaction becomes **less spontaneous** and the **reaction potential decreases**.

The actual change in reaction potential is calculated using the **Nernst Equation**

As was the case with free energy, it is possible to calculate the voltage under non-standard conditions.

This is done via the **Nernst equation**:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nf} \ln Q$$

where Q is the reaction quotient. Note: make sure that you don't include solids or liquids in Q

Because you can separate chemical reactions in an electrochemical cell, it is possible to create what is known as a concentration cell, where each half cell contains the same metal/ion, just with solutions of differing concentration.

For instance, if you took the cell: Cu | Cu²⁺ (0.1 M) || Cu²⁺ (1.0 M) | Cu, E[°]_{cell} would be zero, but Q = 0.1/1.0 = 10, so E_{cell} = 0.03 V.

Any time you see a voltaic cell question and the concentrations are not 1 M, it's telling you to use the Nernst Equation.